

**PATENT**

**451-Div.**

**APPLICATION FOR UNITED STATES LETTERS PATENT**

**for**

**POLISHING SLURRIES FOR COPPER  
AND ASSOCIATED MATERIALS**

**by**

**William A. Wojtczak, Thomas H. Baum, Long Nguyen, and Cary Regulski**

## BACKGROUND OF THE INVENTION

The present invention relates to a chemical mechanical polishing slurry for surfaces of a semiconductor wafer, and more particularly, to a chemical mechanical polishing slurry and a method for using the slurry to remove and polish copper, barrier materials and dielectric materials layered on semiconductor wafer surfaces.

Semiconductor wafers are used to form integrated circuits. The semiconductor wafer typically includes a substrate, such as silicon, upon which dielectric materials, barrier materials, and metal conductors and interconnects are layered. These different materials have insulating, conductive or semi-conductive properties. Integrated circuits are formed by patterning regions into the substrate and depositing thereon multiple layers of dielectric material, barrier material, and metals.

In order to obtain the correct patterning, excess material used to form the layers on the substrate must be removed. Further, to obtain efficient circuits, it is important to have a flat or planar semiconductor wafer surface. Thus, it is necessary to polish certain surfaces of a semiconductor wafer.

Chemical Mechanical Polishing or Planarization ("CMP") is a process in which material is removed from a surface of a semiconductor wafer, and the surface is polished (planarized) by coupling a physical process such as abrasion with a chemical process such as oxidation or chelation. In its most rudimentary form, CMP involves applying slurry, a solution of an abrasive and an active chemistry, to a polishing pad that buffs the surface of a semiconductor wafer to achieve the removal, planarization, and polishing process. It is not desirable for the removal or polishing process to be comprised of purely physical or purely chemical action, but rather the synergistic combination of both in order

1 to achieve fast uniform removal. In the fabrication of integrated circuits, the CMP slurry  
2 should also be able to preferentially remove films that comprise complex layers of metals  
3 and other materials so that highly planar surfaces can be produced for subsequent  
4 photolithography, or patterning, etching and thin-film processing.

5 Recently, copper has been used as the metal interconnect for semiconductor  
6 wafers. Typically for copper technology, the layers that are removed and polished  
7 consist of a copper layer (about 1-1.5  $\mu\text{m}$  thick) on top of a thin copper seed layer (about  
8 0.05-0.15  $\mu\text{m}$  thick). These copper layers are separated from the dielectric material  
9 surface by a layer of barrier material (about 50-300  $\text{\AA}$  thick). The key to obtaining good  
10 uniformity across the wafer surface after polishing is by using a slurry that has the correct  
11 removal selectivities for each material. If appropriate material removal selectivity is not  
12 maintained, unwanted dishing of copper and/or erosion of the dielectric material may  
13 occur.

14 Dishing occurs when too much copper is removed such that the copper surface is  
15 recessed relative to the dielectric surface of the semiconductor wafer. Dishing primarily  
16 occurs when the copper and barrier material removal rates are disparate. Oxide erosion  
17 occurs when too much dielectric material is removed and channels are formed in the  
18 dielectric material on the surface of the semiconductor wafer relative to the surrounding  
19 regions. Oxide erosion occurs when the dielectric material removal rate is locally much  
20 higher than the copper removal rate. Dishing and oxide erosion are area dependent being  
21 wafer pattern and pitch dependent as well.

22 Typical commercial CMP slurries used to remove overfill material and polish  
23 semiconductor wafer surfaces have a barrier material removal rate below 500  $\text{\AA}/\text{min}$ .

1 Further, these slurries have a copper to barrier material removal rate selectivity of greater  
2 than 4:1. This disparity in removal rates during the removal and polishing of the barrier  
3 material results in significant dishing of copper on the surface of the semiconductor wafer  
4 and/or poor removal of the barrier material.

5 Another problem with conventional CMP slurries is that the removal chemistry of  
6 the slurry is compositionally unstable. Further, many of the colloidal abrasives  
7 agglomerate after relatively short time frames following addition to the supporting  
8 chemistry. Both of these problems lead to significant operational obstacles.

9 A further problem in commercial CMP slurries is that the abrasive materials in the  
10 slurries produce defects in the form of micro scratches. These slurries also have poor  
11 planarization efficiency, which is the ability of the slurry to polish high points  
12 preferentially over low points on the surface of the wafer. Micro scratches and poor  
13 planarization efficiency result in integrated circuits with increased defects and a lower  
14 yield.

15 Still another problem of commercial CMP slurries is that the chemicals that make  
16 up the slurries produce a copper surface that has a high corrosion tendency post polish.

17 An object of this invention, therefore, is a CMP slurry that employs a two-step  
18 slurry approach. The slurry used in the first step has a high copper removal rate and a  
19 comparatively low barrier material removal rate. The slurry used in the second step has a  
20 relatively high barrier material removal rate, comparable removal rate for copper and low  
21 removal rate on the dielectric material. By using this two-step slurry approach, the first  
22 and second slurries can provide the appropriate selectivity ranges to minimize copper

1 dishing and oxide erosion, thereby providing a viable CMP approach to advanced device  
2 manufacturing.

3 Another object of the invention is for the first and second slurries to have stable  
4 removal chemistry.

5 Yet another object is to use abrasives in the first slurry that achieve high copper  
6 removal rates, but minimal barrier material removal rates, and to use abrasives in the  
7 second slurry that provide superior removal rates on barrier material and low removal  
8 rates for copper, which also minimize micro scratch defects and provide very good  
9 planarization efficiency.

10 It is a further object of this invention to employ active copper cleaning chemistry  
11 and corrosion inhibitors in the slurry to minimize copper corrosion post polish, and to  
12 eliminate post-polish cleaning steps.

13 These and other objects and advantages of the invention will be apparent to those  
14 skilled in the art upon reading the following detailed description and upon reference to  
15 the drawings.

## 16 SUMMARY OF THE INVENTION

17 The present invention is directed to a chemical mechanical polishing slurry  
18 comprising a first slurry, which has a high removal rate on copper and a low removal rate  
19 on barrier material and a second slurry, which has a high removal rate on barrier material  
20 and a low removal rate on copper and the associated dielectric material. The first and  
21 second slurries comprise silica particles, an oxidizing agent, a corrosion inhibitor, and a  
22 cleaning agent. Also disclosed as the present invention is a method for chemical  
23 mechanical polishing copper, barrier material and dielectric material with the polishing

1 slurry of the present invention. As will become apparent from the discussion that  
2 follows, the stable slurry and method of using the slurry provide for removal of material  
3 and polishing of semiconductor wafer surfaces with significantly no dishing or oxide  
4 erosion, with significantly no surface defects and good planarization efficiency, and  
5 produce a copper surface with minimal corrosion tendency post-polish.

## 6 BRIEF DESCRIPTION OF THE DRAWINGS

7 **FIG. 1** is a cross-sectional view of a semiconductor wafer prior to chemical  
8 mechanical polishing.

9 **FIG. 2** is a cross sectional view of the semiconductor wafer of **FIG. 1** following  
10 chemical mechanical polishing with the first slurry, according to the present invention.

11 **FIG. 3** is a cross sectional view of the semiconductor wafer of **FIG. 2** following  
12 chemical mechanical polishing with the second slurry, according to the present invention.

13 **FIG. 4** is a cross sectional view of a semiconductor wafer illustrating copper  
14 dishing.

15 **FIG. 5** is a cross sectional view of a semiconductor wafer illustrating oxide  
16 erosion.

17 **FIG. 6** is a transmission electron micrograph (TEM) showing 13 nm silica  
18 particles of the present invention.

19 **FIG. 7** is the size distribution of 13nm silica particles of the present invention  
20 determined with Coulter N4 Plus particle analyzer.

## 21 DETAILED DESCRIPTION OF THE INVENTION

22 **FIG. 1** illustrates a semiconductor wafer **10** prior to CMP. As shown, substrate  
23 **11** may be made of any conventional semiconductor materials, including silicon or

1 germanium or silicon-germanium. Layered on top of the substrate **11** is dielectric  
2 material **12**, which is preferentially silicon oxide, low k dielectrics comprised  
3 substantially of silicon oxide or a carbon containing silicon oxide. The instant invention  
4 is not limited to such dielectric materials and is also useful for removal of dielectrics such  
5 as fluoride doped silicon glass (FSG). Layered on the dielectric material **12**, is barrier  
6 material **13**. The barrier material layer **13** is typically about 50 to 300 Å thick. The  
7 barrier material **13** may be any material conventionally used, but is typically chosen from  
8 the group of tungsten nitride, tantalum, tantalum nitride, titanium nitride, silicon doped  
9 tantalum nitride or silicon doped titanium nitride. Finally, a layer of copper **14** covers the  
10 barrier material layer **13**, and extends into trenches **14a**, **14b**, and **14c**. The copper layer  
11 **14** is usually about 0.1-0.15 µm thick and the copper layer **14** in **FIG. 1** includes a thin  
12 copper seed layer, which is usually about 0.05-0.15 µm thick.

13 The invention is a CMP slurry designed to polish copper **14** and associated barrier  
14 materials **13** such as tungsten nitride, tantalum, tantalum nitride, silicon doped tantalum  
15 nitride, titanium nitride and silicon doped titanium nitride. The chemical mechanical  
16 polishing slurry of the present invention is comprised of two parts. The first slurry is a  
17 copper selective slurry used to remove the bulk copper down to the barrier layer (**FIG. 2**).  
18 The first slurry has a high removal rate of copper and a low removal rate of barrier  
19 material. The second slurry is selective to the barrier layer and removes the barrier  
20 material down to the dielectric material. The barrier and copper rate are comparable for  
21 this step (**FIG. 3**). The various removal rates of the first and second slurries on various  
22 materials are shown in Table 1. In this way, two slurries together comprise a combined  
23 package to polish copper metallization schemes for integrated circuit manufacturing.

Table 1. Removal Rates of the First and Second Slurries on Different Materials\*

LAYER	First Slurry Removal Rates (Å/min)	Second Slurry Removal Rates (Å/min)	Selectivity Material:Cu	
			First Slurry	Second Slurry
Copper	>5000	<1000		
Tantalum	< 500	> 1000	1:10	1:1
Tantalum Nitride	< 500	> 1000	1:10	1:1
Thermal Oxide	< 150	< 150	1:50	1:6

\*(Down Force = 5 psi, Flow Rate = 200 mL/min, Table Speed = 90 rpm, Quill Speed = 50 rpm, Pad Type = IC 1000)

Referring to FIG. 1, the present invention includes a method for chemical mechanical polishing copper 14, barrier material 13 and dielectric material 12, comprises the following steps: (1) providing a first chemical mechanical polishing slurry that has a high removal rate on copper 14 and a low removal rate on barrier material 13; (2) chemical mechanical polishing a semiconductor wafer surface 10 with the first slurry; (3) providing a second chemical mechanical polishing slurry that has a high removal rate on barrier material 13 a comparable removal rate on copper 14 and a low removal rate on the dielectric material 12; and (4) chemical mechanical polishing the semiconductor wafer surface 10 with the second slurry.

Generally, the slurry is applied to a pad contained on a polishing instrument. Polishing instrument parameters such as down force (DF), flow rate (FR), table speed (TS), quill speed (QS), and pad type can be adjusted to effect the results of the CMP slurry. These parameters are important in obtaining efficient planarization results and limiting dishing and erosion. Although these parameters may be altered, when used with



1 the CMP slurry of the present invention, the standard conditions used are DF of 5psi, FR  
2 of 200 mL/min, TS of 90 rpm, QS of 50 rpm, and the IC 1000 pad type.

3 **FIG. 2** illustrates the semiconductor wafer **10** of **FIG. 1**, after steps (1) and (2) of  
4 the present method for CMP have been carried out, and the semiconductor wafer surface  
5 has been polished with the first slurry. When **FIG. 2** is compared to **FIG. 1**, the top  
6 copper layer **14** in **FIG. 1** has been preferentially removed, and only the copper in the  
7 trenches (**FIG. 2**) **18a**, **18b**, and **18c** is left. As shown in **FIG. 2** the barrier material layer  
8 **17** is substantially in tact, and the dielectric material **16** based on substrate **15** is still  
9 unexposed.

10 Similarly, **FIG. 3** illustrates the semiconductor wafer **10** of **FIGS. 1** and **2**, after  
11 steps (3) and (4) of the present method for CMP have been carried out, and the  
12 semiconductor wafer surface has been polished with the second slurry. As shown in  
13 **FIG. 3**, the barrier material layer **21** has been removed down to the dielectric material **20**.  
14 The second slurry also removed just enough of the copper in trenches **22a**, **22b**, and **22c**  
15 so that the surface of the semiconductor wafer **10** is flat and planar. The second slurry  
16 also serves to polish the newly exposed surface, including the dielectric material **20**, the  
17 barrier material **21a**, **21b**, **21c**, and the copper **22a**, **22b**, **22c**. All of these materials are  
18 based on substrate **19**.

19 By using the first and second slurries of the claimed invention, with the  
20 selectivities described in Table 1, and following the described method, copper dishing  
21 (**FIG. 4**) and oxide erosion (**FIG. 5**) can be minimized. **FIG. 4** shows a semiconductor  
22 wafer to which a CMP slurry has been applied, which had a higher selectivity for copper  
23 **26a**, **26b**, **26c** than for the barrier material **25a**, **25b**, **25c** or dielectric material **24**. As a

1 result, disparate amounts of copper are removed from the surface of the semiconductor  
2 wafer. This is known as copper dishing and is shown by the dish-like troughs 27a, 27b,  
3 and 27c in the trenches of copper 26a, 26b, 26c. The CMP slurry of the present invention  
4 and method of using this slurry greatly reduces copper dishing.

5 Similarly, FIG. 5 shows a semiconductor wafer to which a CMP slurry has been  
6 applied, which has a higher selectivity for the dielectric material 29 than for the barrier  
7 material 30a, 30b, 30c, or copper 31a, 31b, 31c. As a result, disparate amounts of  
8 dielectric material are removed from the surface of the semiconductor wafer. This is  
9 known as oxide erosion and is shown by the indentions and/or reduction of the dielectric  
10 material 29a, 29b. The CMP slurry of the present invention and method of using this  
11 slurry greatly reduces oxide erosion.

12 Turning now to the composition of the CMP slurry, generally the first and second  
13 slurries comprise silica particles, an oxidizing agent, a corrosion inhibitor, and a cleaning  
14 agent. The chemistry of the first and second slurries should be stable and have a pH in  
15 the range of about 2 to 5. The first and second slurries may contain potassium or  
16 ammonium hydroxide in such amounts to adjust the pH to a range of about 2 to 5

17 The preferred oxidizing agent for the first and second slurries is potassium iodate  
18 formed by reaction of  $\text{HIO}_3$  with  $\text{KOH}$ . The corrosion inhibitor and cleaning agent for  
19 the first and second slurries should be a carboxylic acid. More specifically, the  
20 carboxylic acid may be chosen from the group of glycine, oxalic acid, malonic acid,  
21 succinic acid and nitrilotriacetic acid. Alternatively, the carboxylic acid may be a  
22 dicarboxylic acid that preferentially has a nitrogen containing functional group. In the  
23 most preferred form, the corrosion inhibitor and cleaning agent for the first and second

1 slurries is iminodiacetic acid. Inorganic acids such as phosphoric, nitric and hydrochloric  
2 were added to adjust pH and accelerate copper removal rates.

3 The use of potassium iodate as the oxidizing agent and carboxylic acids as the  
4 corrosion inhibitors and cleaning agents and inorganic acids as accelerating agents  
5 creates a stable removal chemistry in the pH region of about 2 to 5, for the first and  
6 second slurries. Further, the use of copper corrosion inhibitors and cleaning agents  
7 minimizes copper corrosion, as indicated by low static etch rates of roughly less than 50  
8 Å/min on copper.

9 The silica particles of the first and second slurries can be precipitated. The  
10 precipitated particles usually range from about 3 to 100 nm in size and can be spherical.  
11 An alternative to precipitated silica particles in the first slurry is fumed silica. Generally,  
12 the fumed silica has a mean particle size of less than 700 nm.

13 Alternatively, and more preferred is to use colloidal silica particles of the type  
14 described. The colloidal silica particles can range from about 3 to 100 nm in size, and  
15 can be spherical. Preferentially, when the first and second slurries employ spherical  
16 colloidal particles, the particles should have a narrow size distribution. More  
17 specifically, about 99.9% of the spherical colloidal particles should be within about 3  
18 sigma of a mean particle size with negligible particles larger than about 500 nm.

19 The first slurry, thus, can employ either precipitated spherical silica particles in  
20 the size range of 3 to 100 nm, or fumed silica with mean particle size less than about 700  
21 nm. These particles coupled with the iodate chemistry allows the first slurry to achieve  
22 high copper removal rate but minimal barrier material removal rate. Colloidal silica, with  
23 a narrow size distribution, minimizes micro scratch defects and provides superior

1 removal rates on barrier materials, greater than about 1000 Å/min, and low removal rates  
2 for copper for the second slurry. Further, spherical silica abrasives with a mean size of  
3 less than about 100 nm provide very good planarization efficiency.

4 The pH, oxidizing agents, modifying agents, abrasive particle composition and  
5 size distribution, and weight percent were evaluated to establish a baseline for removal  
6 rates and selectivity.

#### 7 EXAMPLE I

8 Precipitated silica mean particle sizes of 8 nm, 20 nm, and 70 nm were tested.  
9 The fumed silica particle size tested was less than 700 nm. The optimum CMP slurry,  
10 including the first and second slurry, had a precipitated silica mean size of less than about  
11 100 nm. The optimum fumed silica abrasive mean size for the first slurry is less than  
12 about 700 nm. The optimum CMP slurry formulations contain 1-10% precipitated silica,  
13 or fumed silica for the first slurry.

14 Further, different types of abrasive particles were studied to maximize the  
15 removal and selectivity characteristic of the slurry. Precipitated silica abrasives, with  
16 mean size distributions of 4 nm, 8 nm, 13 nm, 20 nm and 70 nm were tested. **FIG. 6**  
17 shows a TEM picture of 13 nm slurry. The size distribution of these particles is  
18 presented in **FIG. 7**. Fumed silica, with a mean particle size of less than about 700 nm,  
19 was also evaluated. All of these mean size distributions can be used to achieve effective  
20 polishing rates and selectivities for the first and second slurries.

#### 21 EXAMPLE 2

22 Different pH ranges were tested for the first and second slurries (See Table 2 and  
23 3). The precipitated silica abrasives had a starting pH range of 9-11 and the fumed silica

had a starting pH range of 2-7. The optimum CMP slurry was found to be acidic. Thus, the pH ranges were altered to the 2 to 5 range by adding potassium, sodium or ammonium hydroxide in appropriate amounts to solutions of iodic acid, cleaning agent and corrosion inhibitor.

### EXAMPLE 3

Several formulations of the first slurries were prepared. The characteristics of these formulations are described in Table 2. The first slurry is optimally comprised of formula 5, for colloidal silica particles, and formula 19 for fumed silica particles. Thus, the first slurry is preferentially comprised of 1-10% colloidal silica with particle size 3 to 100 nm, or 1-5% fumed silica with mean particle size of less than about 700 nm. Further, the active chemistry for the optimum first slurry is about 1-12% potassium iodate ( $KIO_3$ , formed by reaction of  $HIO_3$  with  $KOH$ ), which is used as the oxidizing agent for the copper, about 0-5% concentrated inorganic acid as a copper activating agent, and 0-2% iminodiacetic acid (IDA) as the copper corrosion inhibitor and cleaning agent.

Table 2. Formulations for the First Slurry

Formula	Oxidizer, %	Copper Inhibitor, %	Copper Activator, %	Neutralizer, %	Abrasive, %	pH	Thermal Oxide RR*	Copper RR *	Tantalum RR	Tantalum Nitride RR
1	$HIO_3$ , 8.22	IDA, 1.5	$H_3PO_4$ 1.764	KOH 4.523; $NH_4OH$ , 3.7768	Colloidal (13 nm), 1	2.4	-	3176	-	-
2	$HIO_3$ , 12.33	IDA, 1.5	$H_3PO_4$ 0.5	KOH, 5.022	Colloidal (13 nm), 1	2.7	113	4713	-	-
3	$HIO_3$ , 10	IDA, 1.5	-	$NH_4OH$ , 2.685	Colloidal (13 nm), 1	3.0	126	4800	-	-
4	$HIO_3$ , 10	IDA, 1.5	-	KOH, 4.084	Colloidal (13 nm), 1	2.8	126	5165	-	-
5	$HIO_3$ , 10	IDA, 1.5	$H_3PO_4$ , 0.5	KOH, 4.523	Colloidal (13 nm), 1	2.9	151	6530	453	590
6	$HIO_3$ , 12.33	IDA, 1.5	$H_3PO_4$ , 0.5	KOH, 5.486	Colloidal (13 nm), 1	3.1	115	6877	422	528
7	$HIO_3$ , 12.33	IDA, 1.5	$H_3PO_4$ , 0.5	KOH, 5.486	Colloidal (13 nm), 1	3.1	115	6877	422	528

Formula	Oxidizer, %	Copper Inhibitor, %	Copper Activator, %	Neutralizer, %	Abrasive, %	pH	Thermal Oxide RR*	Copper RR *	Tantalum RR	Tantalum Nitride RR
					1					
8	HIO <sub>3</sub> , 8.22	IDA, 1.5	H <sub>3</sub> PO <sub>4</sub> , 0.5	KOH, 3.978	Colloidal (13 nm), 1	3.1	112	4797	494	730
9	HIO <sub>3</sub> , 8.22	-	HCl, 0.15g	KOH, 4.284	Colloidal (13 nm), 1	6.0	117	423	878	1031
10	HIO <sub>3</sub> , 4.11	IDA, 1.5	H <sub>3</sub> PO <sub>4</sub> , 0.5	KOH, 2.92	Colloidal (13 nm), 1	3.4	134	2138	550	618
11	HIO <sub>3</sub> , 4.11	IDA, 1.5	H <sub>3</sub> PO <sub>4</sub> , 0.5	KOH, 2.92	Colloidal (13 nm), 1	3.6	105	2134	512	882
12	HIO <sub>3</sub> , 6.17	IDA, 1.5	H <sub>3</sub> PO <sub>4</sub> , 0.5	KOH, 4.087	Colloidal (13 nm), 1	6.0	106	1448	890	1047
13	HIO <sub>3</sub> , 4.11	IDA, 1.5	H <sub>3</sub> PO <sub>4</sub> , 0.5	KOH, 2.918	Colloidal (13 nm), 1	3.5	140	3900	720	1066
14	HIO <sub>3</sub> , 4.11	IDA, 1.5	H <sub>3</sub> PO <sub>4</sub> , 0.5	KOH, 3.012	Colloidal (8 nm), 1	3.6	45	4157	527	623
15	HIO <sub>3</sub> , 4.11	IDA, 1.5	H <sub>3</sub> PO <sub>4</sub> , 0.5	KOH, 3.067	Colloidal (20 nm), 1	3.7	172	6852	649	842
16	HIO <sub>3</sub> , 4.11	IDA, 1.5	H <sub>3</sub> PO <sub>4</sub> , 0.5	KOH, 3.13	Colloidal (70 nm), 1	3.6	171	2720	451	625
17	HIO <sub>3</sub> , 4.11	IDA, 1.5	H <sub>3</sub> PO <sub>4</sub> , 0.5	KOH, 2.918	Colloidal (13 nm), 1	3.6	118	3973	832	1028
18	HIO <sub>3</sub> , 4.11	IDA, 1.5	-	KOH, 2.474	Colloidal (13 nm), 1	3.5	167	5630	728	946
19!	HIO <sub>3</sub> , 4.11	IDA, 1.5	H <sub>3</sub> PO <sub>4</sub> , 0.5	KOH, 2.918	fumed, 1	3.6	15	4823	2.4	-10

\* "RR" means removal rates in Å/min.

Stock Solutions: HIO<sub>3</sub> (50% by weight); H<sub>3</sub>PO<sub>4</sub> (85.87% by weight); KOH (45-46% by weight);  
NH<sub>4</sub>OH (28-30% by weight); HNO<sub>3</sub> (68-70% by weight); HCl (36-38% by weight)

As can be seen from Table 2, all of the first slurry formulations of the present invention were effective in achieving acceptable copper removal rates, and semiconductor wafer surfaces of high quality. Thus, the first slurry is preferentially comprised of 1-10% colloidal silica with particle size of less than about 100 nm.

#### EXAMPLE 4

Several formulations of the second slurry were prepared. The characteristics of these formulations are described in Table 3. The second step slurry is dependent on the copper removal rate requirement and therefore is optimally comprised of either formula 6 or 9.

The active chemistry for the optimum second slurry is 0.1-1% potassium iodate ( $\text{KIO}_3$ , formed by reaction of  $\text{HIO}_3$  with  $\text{KOH}$ ) as the oxidizing agent for the copper, 0-5 % concentrated inorganic acid and 0-2% iminodiacetic acid as the copper corrosion inhibitor and cleaning agent. Table 3. Formulations for the Second Slurry

Formula	Oxidizer, %	Copper Inhibitor, %	Copper Activator, %	Neutralizer, %	Abrasive, %	pH	Thermal Oxide RR*	Copper RR *	Tantalum RR	Tantalum Nitride RR
1	$\text{HIO}_3$ , 0.1	IDA, 1.5	-	$\text{KOH}$ 1.005	Colloidal (13 nm), 1	3.4	101	430	462	2128
2	$\text{HIO}_3$ , 0.1	IDA, 1.5	$\text{HNO}_3$ , 10	$\text{KOH}$ 13.66	Colloidal (13 nm), 1	3.0	100	572	146	1749
3	$\text{HIO}_3$ , 0.1	IDA, 0.1	$\text{HNO}_3$ , 5; $\text{HCl}$ , 5	$\text{KOH}$ 13.14	Colloidal (13 nm), 1	3.0	53	358	50.21	751
4	$\text{HIO}_3$ , 0.1	IDA, 1.5	$\text{H}_3\text{PO}_4$ , 1.5	$\text{KOH}$ 2.079	Colloidal (13 nm), 1	2.7	116	574	772	1471
5	$\text{HIO}_3$ , 0.1	IDA, 1.5	$\text{HNO}_3$ , 2	$\text{KOH}$ 3.674	Colloidal (13 nm), 1	3.1	149	511	670	2087
6	$\text{HIO}_3$ , 0.1	IDA, 1.5	$\text{HNO}_3$ , 2.31	$\text{NH}_4\text{OH}$ , 2.507	Colloidal (13 nm), 1	3.1	130	239	623	2146
7	$\text{HIO}_3$ , 0.1	IDA, 1.5	-	$\text{KOH}$ , 1.312	Colloidal (13 nm), 1	3.4	126	1053	657	1200
8	$\text{HIO}_3$ , 0	IDA, 2	-	$\text{KOH}$ , 1.305	Colloidal (13 nm), 1	3.5	200	0	> 3000	217
9	$\text{HIO}_3$ , 0.5	IDA, 1.5	-	$\text{KOH}$ , 1.086	Colloidal (13 nm), 1	3.5	120	1120	731	907
10	$\text{HIO}_3$ , 1.5	IDA, 1.5	-	$\text{KOH}$ , 1.443	Colloidal (13 nm), 1	3.5	131	1208	901	856

\* "RR" means removal rates in  $\text{\AA}/\text{min}$ .

Stock Solutions:  $\text{HIO}_3$  (50% by weight);  $\text{H}_3\text{PO}_4$  (85.87% by weight);  $\text{KOH}$  (45-46% by weight);  $\text{NH}_4\text{OH}$  (28-30% by weight);  $\text{HNO}_3$  (68-70% by weight);  $\text{HCl}$  (36-38% by weight).

As can be seen from Table 3, all of the second slurry formulations of the present invention were effective in achieving acceptable barrier dielectric and copper removal rates, and semiconductor wafer surfaces of high quality.

The first and second slurries described herein, may also be used in a method of chemical mechanical polishing as described above. Also, while this invention has been disclosed and discussed primarily in terms of specific embodiments thereof, it is not

greater rate than copper with an oxidizing agent/corrosion inhibitor weight ratio of less than one. Kaufman thus fails to teach or suggest applicants' claimed invention.

Because there is no motivation or suggestion in Kaufman to modify the CMP process to yield applicants' claimed invention, and because Kaufman fails to disclose or provide any derivative basis for applicants' claimed invention, the Examiner is respectfully requested to withdraw the rejection of claim 1 under 35 U.S.C. §103(a) based on Kaufman.

In the alternative, the Examiner has rejected claim 1 under 35 U.S.C. §103(a) as being unpatentable over Kaufman in view of Farkas. Applicants vigorously disagree.

Farkas teaches a two-step CMP process wherein the first step preferentially polishes copper and the second step preferentially polishes barrier material. The slurry utilized in the second step of the CMP process comprises an abrasive and an amine with an overall preferred pH of 9-11 (see Farkas, col. 7, line 38).

Referring to the July 15, 2003 Office Action, the Examiner stated the following (see page 6, lines 6-17):

“Kaufman makes no mention of the polishing rate of barrier material in the first CMP slurry. However, it is expected to have “low removal rate” in the absence of any evidence showing the contrary. Although Kaufman is silent about the polishing rate of the second slurry for the dielectric layer, it is expected to have “low removal rate” in the absence of any evidence showing the contrary since there is no numerical value for the removal rates (“low” or “high”) is defined. In alternative, Farkas teaches two-step CMP polishing for copper and barrier material. The first slurry is used to polish copper, the second slurry is used to polish the barrier faster than the dielectric or the copper (abstract). Farkas teaches numerical values for the removal rates, which are consistent with the criteria of each slurry according to Kaufman. Hence, it would have been obvious to one of ordinary skill in the art to incorporate Farkas in to the process of Kaufman because both are used for the same purpose (two step copper/barrier CMP).”

Thus, what the Examiner seems to be proposing is that the combination of the first step of Kaufman with the second step of Farkas replicates applicants' claimed invention. Applicants vigorously disagree.

The Examiner is reminded that the limitations of the cited prior art references, as a whole, must be considered. The Examiner cannot selectively focus on isolated individual elements of the primary and secondary references, while simultaneously overlooking other elements taught to be utilized and necessary by the respective references. Considering Farkas as a whole, even though the second slurry is



formulated to polish the barrier material faster than copper, the second slurry, comprising an abrasive and an amine at a pH of 9-11, is fundamentally different from and non-suggestive of applicants' claimed slurry composition. The Examiner is reminded that applicants' second slurry comprises an abrasive, an oxidizing agent and a corrosion inhibitor at a pH of about 2 to about 4.

The combination of Kaufman and Farkas therefore fails to teach or suggest applicants' claimed invention. Accordingly, applicants respectfully request that the rejection of claim 1 under 35 U.S.C. §103(a) based on Kaufman and Farkas be withdrawn.

**Fees Payable for Added Claim and Terminal Disclaimer**

The fee for the net addition of one (1) independent claim herein is \$86.00. The fee for the concurrently submitted Terminal Disclaimer is \$110. A check payable to Commissioner for Patents in the amount of \$196 is enclosed for such added independent claim and Terminal Disclaimer fee.

Any additional fee or charge determined to be properly payable in connection with the entry of this amendment is hereby authorized to be charged to Deposit Account No. 08-3284 of Intellectual Property/Technology Law.

**Section III. CONCLUSION**

Based on the amendments made herein and the foregoing remarks, claims 1-33, 38-45 and 50-57 are now in form and condition for allowance. The Examiner therefore is respectfully requested to reconsider and allow such amended claims.

Respectfully submitted,



---

Steven J. Hultquist  
Reg. No. 28,021  
Attorney for Applicants

**INTELLECTUAL PROPERTY/  
TECHNOLOGY LAW**  
P.O. Box 14329  
Research Triangle Park, NC 27709  
Telephone: (919) 419-9350  
Fax: (919) 419-9354  
Attorney Ref: 2771-451 DIV (7486)

